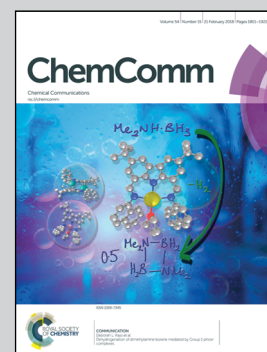**Showcasing research by P. Bauduin and co-workers from the Marcoule Institute of Separation Chemistry (ICSM), University of Regensburg and Sorbonne Universités**

Polyoxometalates in the Hofmeister series

A simple experimental procedure based on the cloud point measurement of a non-ionic surfactant is proposed as a tool to classify polyoxometalates (POMs) in the Hofmeister series according to their affinity to adsorb on neutral polar surfaces. The strength of adsorption of super-chaotropic POMs is modulated by their charge density.

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Polyoxometalates in the Hofmeister series†

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We propose a simple experimental procedure based on the cloud point measurement of a non-ionic surfactant as a tool for (i) estimating the super-chaotropic behaviour of polyoxometalates (POMs) and for (ii) establishing a classification of POMs according to their affinity towards polar surfaces.

Polyoxometalates (POMs) are discrete nanometer sized anionic oxo-metal clusters that consist of early transition metals, especially V, Mo, and W and often incorporate a heteroatom.[1,2] Due to their unique structural and electronic versatility, POMs find many applications in biology,[3–6] as a phasing tool in protein crystallography,[7] as (photo)-catalytically active oxidants[8,9] and in molecular materials.[10–13]

According to Hofmeister's classification of ions, chaotropic or salting-in anions are hydrated, highly polarizable, with low charge density and have the propensity to weakly adsorb on polar interfaces.[14–18] Furthermore, they are usually referred to as soft anions. Recently, Naskar *et al.* showed that POMs are super-chaotropes compared to classical chaotropic anions, such as iodide or thiocyanate, mostly due to their large size and delocalized charge.[19] Naskar *et al.* also highlighted that the super-chaotropic character of POMs was related to their strong propensity to adsorb on electrically neutral surfaces covered with polar groups such as $-(O-CH_2-CH_2)_x-OH$ or glucoside groups.[19] The POM adsorption process is considered to be entropically driven by partial dehydration of both the surfaces and POMs. It was further shown that the adsorption of super-chaotropic POMs is not specific towards polar surfaces but can be generalized to neutral and hydrated oligomers or polymers such as (poly-)ethylene glycol.[20] In most of the applications of

POMs surface effects are involved as in catalysis,[21] materials science,[22] in micrography[23] and in the fabrication of electrodes.[24] Therefore, a deep understanding and characterization of the ability of POMs to adsorb spontaneously on the surfaces is essential for further innovative developments.

In this contribution, we propose a simple experimental procedure to classify POMs according to their propensity to adsorb on polar surfaces. The classification of POMs was made by investigating the cloud point (CP) increase of a non-ionic ethylene glycol (EO_x)-based surfactant, tetraethylene glycol octyl ether (C_8EO_4), upon the addition of POMs of different sizes, charges, structures and compositions (see Fig. 1). The term cloud point generally refers to a liquid–liquid phase separation upon heating an aqueous solution containing a thermosensitive polymer or a surfactant.[25,26] The CP increase of a thermo-responsive molecule by adding a salt has been previously used as a tool to evaluate the adsorption strength/association constant of polarizable anions to the thermo-responsive molecule.[26,27]
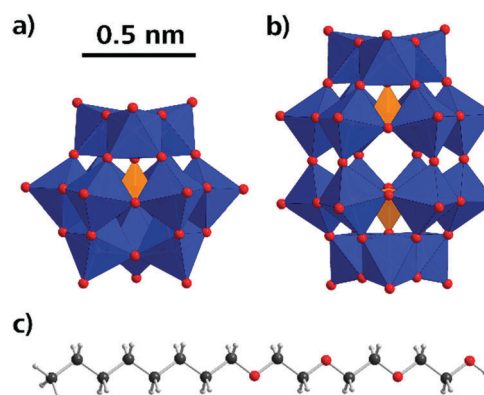
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Fig. 1 Representative structures of (a) an α-Keggin-type POM anion (here $PW_{12}O_{40}{}^{3-}$, HPW, $PMo_{12}O_{40}{}^{3-}$, HPMo, $SiW_{12}O_{40}{}^{4-}$, HSiW), (b) a Dawson-type POM anion (here $P_2W_{18}O_{62}{}^{6-}$, KP2W and HP2W, and $P_2W_{17}VO_{62}{}^{7-}$, HP2WV) and (c) the structure of tetraethylene glycol monooctyl ether (C_8EO_4).

Naskar et al. showed that a pronounced increase in the CP of C_8EO_4 upon the addition of POMs was related to the strong adsorption of $PW_{12}O_{40}{}^{3-}$ and $SiW_{12}O_{40}{}^{4-}$ anions onto the micellar surface.[19] This approach is extended here to a series of POMs in order to highlight the pertinent parameters that influence the super-chaotropic behaviour of POMs. In a recent work by Kobayashi et al. a partial ranking of POMs according to their chaotropic nature was made based on the effect of POMs on the surface pressure isotherm of ionic and zwitterionic lipids. They concluded that POM's effects result from hydrophobic and electrostatic interactions between polyoxometalates and lipid monolayers.[28] The present work investigates the effect of POMs on non-ionic systems which allows excluding the role of pure electrostatic interactions in the adsorption of POMs at surfaces. Moreover, the role of the hydrophobic effect is also likely to be negligible in the surface adsorption of POMs as they do not show any surface activity at water–alkane interfaces.

The CP increase of C_8EO_4 (60 mM) is plotted in Fig. 2 as a function of POM concentration and compared to the effect of classical Hofmeister anions (data for salts are taken from ref. 19). HPW demonstrates the strongest CP increase followed by HPMo depicting a similar but slightly less pronounced CP increase for c(HPW/HPMo) < 5 mM. For c(HPW/HPMo) > 5 mM, a precipitate is obtained confirming the stronger attractive interactions of these two POMs with the micellar surface, compared to the other investigated POMs. The CP increase by HSiW is even less prominent than the one by HPW and HPMo. Interestingly, KP2W and HP2W, two Dawson-type POMs, increase the CP almost similarly but much less than the Keggin-type POMs. KP2WV displays the least pronounced effect. It is shown here for the first time that POMs of Dawson's type increase the CP of a thermo-sensitive molecule. The CP increase by lowly charged Keggin-type POMs, i.e. HPW, HPMo and HSiW, is more pronounced than by highly charged Dawson-type POMs, i.e. KP2W, HP2W and KP2WV. Moreover, it should be remarked that the CP increase by POMs is much more pronounced than by chaotropic anions in the classical
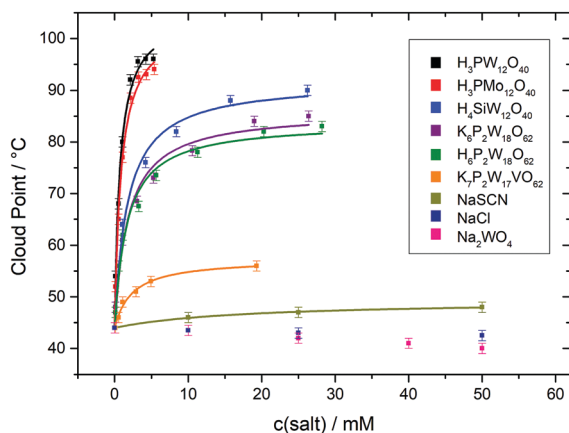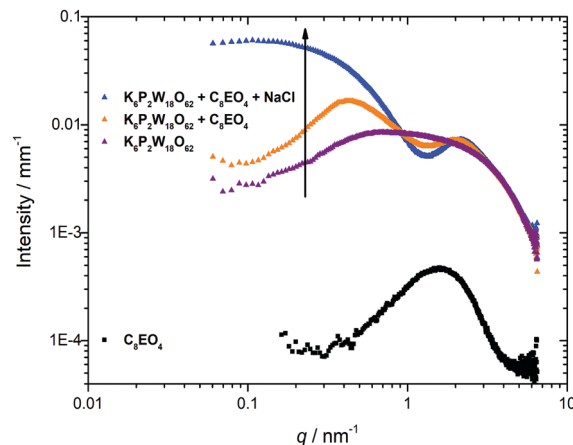

Fig. 3 SAXS spectra of 60 mM C_8EO_4 (with and without 100 mM NaCl), 1 mM $K_6P_2W_{18}O_{62}$ and their mixtures (1 mM $K_6P_2W_{18}O_{62}$–60 mM C_8EO_4 and 1 mM $K_6P_2W_{18}O_{62}$–60 mM C_8EO_4–100 mM NaCl) in aqueous solution.

Hofmeister's series. For example sodium thiocyanate, NaSCN, increases the CP only by 5.3 °C for c(NaSCN) = 50 mM,[19] compared to 10–60 °C for c(POM) = 4 to 8 mM depending on the POM. The ranking according to the absolute CP increase is therefore as follows: HPW > HPMo > HSiW > KP2W ≈ HP2W > KP2WV ⋙ NaSCN.

Small angle X-ray scattering measurements (SAXS) were performed on C_8EO_4, POMs and their mixtures to investigate the adsorption of POMs on the micellar surface, see the results for C_8EO_4–KP2W in Fig. 3. The scattered intensity of 60 mM C_8EO_4 is very low, as expected from the very low contrast of micelles compared to water.[19] The large oscillation, centred at around 1.5 nm^{-1}, originates mainly from an electron density excess in the micellar shell due the presence of EO groups providing a high electron density compared to the micellar core (octyl chains) and water. KP2W displays the scattering signature of dispersed prolate spheroidal objects in aqueous solution with electrostatic repulsions as indicated by the decay of the scattered intensity for q < 0.5 nm^{-1}. The SAXS spectrum of the mixture of 60 mM C_8EO_4 and 1 mM KP2W displays a much higher scattered intensity and a typical pattern of a core–shell structure with a large electron density excess in the shell, i.e. C_8EO_4 micelles with POMs adsorbed in the micellar shell.[19] Strong inter-micelle and inter-POM repulsions account for the depression of the scattered intensity for q < 0.4 nm^{-1}. The addition of 100 mM NaCl to a solution containing 60 mM C_8EO_4 and 1 mM KP2W, aiming at screening electrostatic interactions, leads to an increase in the scattering intensity for q < 0.4 nm^{-1}. Such a SAXS pattern therefore shows the strong adsorption of POMs onto the surface of C_8EO_4 micelles as shown previously by Naskar et al. for HSiW–C_8EO_4 in comparable compositions.[19] The adsorption of POMs onto the surface of C_8EO_4 micelles leads to a strong increase in micelle–micelle repulsions leading to an increased CP of C_8EO_4 in the presence of POMs. A similar conclusion is made for all POMs under discussion since they produce a similar scattering pattern as depicted in Fig. 3, see Fig. S4 (ESI†). The adsorption

Fig. 2 CP of 60 mM C_8EO_4 as a function of increasing POM (or salt) concentration. The solid lines represent Langmuir fits of the CP increase. Error bars represent the error of the CP by detection with visual inspection, ±1 °C. The CP values for salts were taken from ref. 19.

of POMs in the micelle's corona is confirmed by the fitting of the SAXS spectra using a core–shell model, as described previously.[19] The fitting results, see Table S1 (ESI†), suggest a large increase in electron density subsequent to the POM adsorption. Specific details on the fitting procedure are given in the ESI.†

Considering that POMs adsorb on the micellar surface, the CP increase as shown in Fig. 2 resembles a general evolution of an adsorption isotherm. Hence, the CP curves were fitted with a Langmuir model modified by a scaling parameter B_{max} corresponding to the extent of the CP increase:

$$CP = CP_{C_8EO_4} + \frac{B_{max} \times K_A[POM]}{1 + K_A[POM]} \qquad (1)$$

with $CP_{C_8EO_4}$ being the cloud point of C_8EO_4 in pure water and K_A the equilibrium association constant of the adsorption in units of mM^{-1}. This latter parameter is mostly dependent on the steepness of the CP increase at low POM concentrations whereas B_{max} describes the maximum extent of the CP increase. At this point we want to emphasize that the CP evolution does not meet the requirements of a classical Langmuir isotherm model as it (i) implies an adsorption process that is based on a well-defined flat monolayer under isothermal conditions with (ii) identical and equivalent adsorption sites and (iii) excluding (electrostatic) interactions and steric hindrance between POMs on adjacent adsorption sites. Despite the apparent non-applicability of this model on the system studied here, B_{max} and K_A values can be extracted from the best fits of the experimental data, see the fits represented by full lines in Fig. 2. B_{max} and K_A values corresponding to the best fits are listed in Table 1. Both B_{max} and K_A values provide an estimation of the chaotropic behaviour of each POM, i.e. the higher the K_A or B_{max} the stronger the super-chaotropic behaviour. It should be noted that B_{max} values are more reliable than K_a values to estimate the relative chaotropic behaviour of POMs. K_a values are tainted with a large error, typically ± 0.1 mM^{-1}, due to the steep increase in the CP for low POM concentrations observed for all POMs, except for KP2WV which shows a significantly lower B_{max} value. Nevertheless, the low K_a values obtained here – in the mM^{-1} range – show a strong general affinity of the POMs towards the micelle surface. Note that the K_a value for thiocyanate (SCN^-), a classical chaotropic Hofmeister anion, obtained from a similar fitting procedure, is much weaker than that for the (super-chaotropic) POMs, see Table 1.

Table 1 Fitting parameters (R^2 always larger than 98.3%) obtained from a modified Langmuir model of the CP increase, see eqn (1). The volume charge density ρ is obtained by dividing the excess charge by the volume of Keggin type POMs (0.46 nm³) and Dawson type POMs (0.68 nm³) extracted from S. Herrmann[31]

	B_{max} (°C)	K_A (mM^{-1})	Charge (e^-)	ρ (e^- nm^{-3})
$H_3PW_{12}O_{40}$	61.2	1.41	3	6.5
$H_3PMo_{12}O_{40}$	59.6	1.16	3	6.5
$H_4SiW_{12}O_{40}$	47.8	0.58	4	8.7
$K_6P_2W_{18}O_{62}$	42.0	0.56	6	8.8
$H_6P_2W_{18}O_{62}$	39.8	0.61	6	8.8
$K_7P_2W_{17}VO_{62}$	13.4	0.42	7	10.3
NaSCN	5.3	0.06	1	—

In the following an attempt was made to rationalize the series of POMs obtained according to their super-chaotropic behavior. In general, the chaotropic/cosmotropic behavior of ions follows their size/charge and polarizability where large anions of low charge density and high polarizability show the most pronounced chaotropic character.[29] Therefore, the volume charge density of POMs, ρ, expressed in number of charges per volume unit, see Table 1, was chosen as a criterion to characterize the chaotropic behaviour of POMs as ρ is related to their charge and size. It should be noted that for small ions (Cl^-, Br^-, SCN^-, etc.) such a calculation is much trickier since their ion radius in aqueous solutions is not well defined. This leads to huge errors in the estimation of the ionic volume. For this reason hydrated volumes obtained from density measurements are usually considered as a size criterion to compare ions in solution.[30] As POMs are well defined nano-building units their volumes were calculated from their size in the crystal structure. The Keggin type POMs were considered to be oblate spheroids, almost spherical, with dimensions of 0.82 nm × 1.03 nm × 1.03 nm resulting in a volume of 0.46 nm³ and Dawson type POMs were considered as prolate spheroids with dimensions of 1.22 nm × 1.03 nm × 1.03 nm resulting in a volume of 0.68 nm³. These size values were taken from ref. 31, with HPW taken as a representative of a Keggin anion and HP2W as a representative of a Dawson anion. The substitution of tungsten by molybdenum has a negligible influence on the volume of the POM resulting in a similar ρ value for PMo^{3-} and PW^{3-}.

It appears here that the ρ values of POMs are related to the CP increase and to their chaotropy, i.e. the lower the ρ the higher the B_{max}, see Table 1. Indeed, ρ vs. B_{max} shows a roughly linear evolution, with a coefficient of determination of $R^2 = 0.85$ (see Fig. S5, ESI†). This result suggests that the charge density is a major feature of POMs that controls their chaotropic behaviour. It is generally assumed that a higher ρ leads to stronger hydration, i.e. water molecules bind more strongly to POMs with a higher charge density. Consequently, partial dehydration of POMs, taking place along with the adsorption process, is associated with a higher energy cost for POMs with a higher ρ. It is interesting to remark that the type of the POM counterion is negligible on B_{max}, when compared to KP2W and HP2W. Therefore, the counter ion has nearly no influence on the super-chaotropic behaviour of POMs. Moreover, this result is a direct proof that (i) the CP increase of C_8EO_4 by adding POMs is not related to the acidity of different POMs and that (ii) the high acidity does not lead to protonation of the surfactant and formation of an anionic (POM)–cationic (protonated surfactant) complex.

PW^{3-} is found to be slightly more chaotropic than PMo^{3-}, see Table 1 and Fig. 1. PMo^{3-} and PW^{3-} only differ with respect to their polarizability, as they have an almost identical size and the same charge. Indeed, PW^{3-} is known to be more polarizable than PMo^{3-},[32] as expected from the higher number of electrons of a W atom ($Z_W = 74$) compared to a Mo atom ($Z_{Mo} = 42$). Highly polarizable ions adjust their charge distribution to minimize the electrostatic self-energy cost during adsorption

at an interface.[33] Hence, the polarizability of POM nano-ions also influences the chaotropic behaviour and adsorption propensity of POMs towards polar molecules or surfaces but much less pronounced than their charge density.

In an attempt to draw general conclusions, it appears that the super-chaotropic behaviour of anions emerges from different features: the anion should have delocalized charges and should be large enough, typically at least in the nm range (nano-ions), to provide a high entropic gain associated with the surface adsorption process. This major entropic contribution to adsorption is associated with the release of hydration water molecules from the nano-ion (and from the surface) to the water bulk phase. The strength of the super-chaotropic behaviour is related to the volume charge density, ρ of the anion, $i.e.$ the lower the ρ the higher the B_{max}. A stronger anion hydration, due to a higher ρ, leads to a less efficient dehydration (lower entropy gain) during the adsorption process because a smaller number of water molecules is released, see PW^{3-} $vs.$ SiW^{4-} or PW^{3-} $vs.$ $P2W^{6-}$. The anion polarizability influences the chaotropic tendency of POMs (PMo^{3-} $vs.$ PW^{3-}) to a much smaller extent as they scale with dispersion forces which are often proposed to be the driving force of specific ion effects.[29] In this context, our conclusions are also an extension of Collins' concept of matching water affinities, observed between two oppositely charged particles (ions),[34] to the interaction of charged particles (here POMs) with uncharged but hydrated/polar molecules or surfaces. The procedure described here for POMs can be extended to other types of nanoions, such as boron clusters: dodecaborate, which was recently described as a super-chaotrope,[35] or metallacarboranes.[36]

Conflicts of interest

There are no conflicts to declare.

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